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(54) Title: POLYPROPYLENE-CLAY COMPOSITE AND PRODUCING METHOD THEREOF

(57) Abstract: The present invention relates to polypropylene-clay composite comprising (a) denatured polypropylene which contains a functional group, 10~30 wt %; (b) organic layered clay which is connected to the functional group of denatured polypropylene, 10~20 wt %; and (c) polyolefin resin matrix in which the denatured polypropylene and organic layered clay are diffused, 50~98wt %.

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POLYPROPYLENE-CLAY COMPOSITE AND
PRODUCING METHOD THEREOF

Technical Field

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The present invention relates, in general, to a polypropylene-organic clay composite and a method for manufacturing the same, in detail, to a polypropylene-organic clay composite prepared by dispersing an organic
10 layered clay mineral in a polymer resin to complement the disadvantages of conventional inorganic filler, intensifier or filling composite with a particle size of 1 μm or more, and a method for manufacturing the same.

15

Background Art

Typically, inorganic materials such as talc, mica, etc. are used to improve mechanical properties of polyolefin resins. Conventionally, the incorporation of
20 polyolefin resin with such inorganic materials has resorted to mechanical means. However, conventional mechanical incorporation frequently results in poor dispersions in which particles of the inorganic materials form multi-layered aggregates because they are
25 incompatible with polyolefin matrixes.

Various attempts have been made, so far, to improve the dispersibility of inorganic materials in polyolefin resin by making inorganic layered compounds exist as

nano-sized unit layers in the polymer matrixes. In these attempts, it is known that organic substances such as monomers or polymers cannot fully penetrate an interlayer space of inorganic layered materials and unit layers of inorganic layered materials cannot be uniformly dispersed in polymer matrixes without treating a surface of inorganic layered materials with organophilic materials.

For example, USP 4,889,885 discloses a technology for uniformly dispersing inorganic layered materials in polymer resin, in which sodium or potassium ions, naturally existing between unit layers of multi-layered fine-particular materials such as inorganic silicate, are exchanged with onium (e.g. alkyl ammonium ion or functionalized organosilane) and then the layered materials are mixed with monomers or oligomers of the polymer matrix. Cation exchange according to this technology converts hydrophilic silicate into organophilic silicate and broadens the interlayer space of layered materials to improve the dispersibility of inorganic layered materials in polymer resin.

Journal of Appl. Polym. Scien., vol. 55, pp. 119-123(1995) discloses 12-aminolauric acid-treated inorganic silicate for use in the production of polyamide ablation type nano-composites.

In addition, Japanese Patent Publication No. Hei. 10-182892 discloses a method for dispersing layered clay minerals in olefin-based resin matrixes, in which the interlayer space of organic layered clay minerals are

broadened through the intercalation of polyolefinic oligomers with functional groups thereinto, and then the resulting composite materials are mixed with olefin-based resin matrixes.

5 However, dispersibility based mainly on the organization of inorganic layered materials as in the above prior arts is found to be limitedly improved.

Summary of the Invention

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Therefore, it is a feature of the present invention to provide a polypropylene-organic clay composite with greatly improved mechanical properties resulting from the maximizing of compatibility and dispersibility between
15 layered inorganic materials and a polymer matrix by converting the layered inorganic materials such as inorganic silicate into organic materials and by modifying the polymer resin with a certain material so that the layered organic materials can be chemically
20 bonded to a polymer resin matrix, and a method for manufacturing the same.

The present invention provides a polypropylene-organic clay composite comprising (a) a modified polypropylene which contains functional groups, 1.0 to 30
25 wt%, (b) an organic layered clay mineral which is chemically bonded to the functional group of the modified polypropylene, 1.0 to 20 wt%, and (c) a polyolefin resin matrix in which the modified polypropylene and the

organic layered clay mineral are dispersed, 50 to 98 wt%.

Disclosure of the Invention

5 The present invention pertains to a composite comprising a polyolefin matrix in which organic layered clay mineral bonded chemically to modified polypropylene having functional groups is uniformly dispersed.

For use in the present invention, polypropylene is
10 modified with functional group-containing monomers having a highly polar chemical structure. Having a melt index (MI) of 1.0 to 100 g/10 min (ASTM D1238, 230°C), polypropylene suitable as a base for the modified polypropylene of the present invention, is preferably
15 selected from a group consisting of isotactic polypropylene homopolymers, ethylene/propylene copolymers, propylene/ α -olefin non-conjugated diene compound copolymers (e.g. EPDM). As the α -olefin, ethylene, butene-1, heptene-1, hexene-1, and 4-methylpentene may be
20 used alone or in combination. When the melt index of the polypropylene is less than 1.0 g/10 min, the composite is poor in moldability, resulting in low productivity of the molded products. On the other hand, when the melt index is more than 100 g/10 min, the impact strength is
25 drastically reduced.

The highly polar, functional group-containing monomer for modifying polypropylene is unsaturated carboxylic acid or derivatives thereof, exemplified by

maleic anhydride, itaconic anhydride, ditraconic anhydride, oxalic acid, glycidyl methacrylate, carboxylic acid ester, carboxylic acid ether, thiocarboxylic acid, and alkoxy carboxylic acid such as methoxy carboxylic acid or ethoxy carboxylic acid. More preferable is glycidyl methacrylate or maleic anhydride. Glycidyl methacrylate has an epoxide group able to undergo chemical reaction with such nucleophilic groups as hydroxyl groups or carboxylic groups contained in an organic layered clay mineral, in addition to being capable of intercalating the modified polypropylene into the interlayer space of the organic layered clay mineral. As for maleic anhydride, it can chemically react with functional groups such as hydroxyl groups or amino groups contained in the organic layered clay mineral as well as being capable of intercalating the modified polypropylene into the interlayer space of the organic layered clay mineral. The covalent bonding site between polypropylene and the functional group may be a terminal region of the polypropylene molecular chain or any intramolecular region.

In case of modifying polypropylene with the functional group-containing monomers, the monomers may be used alone or in combination. Modified polypropylene can be manufactured by kneading a solution of polypropylene in a suitable organic solvent, along with functional group-containing monomers and a radical generating agent, or through the graft copolymerization of polypropylene,

with functional group-containing monomers in a suitable solvent, in the presence of a radical generator with the use of an extruder.

Preferably, an amount of the unsaturated carboxylic acid or derivatives thereof, used as a modifier for polypropylene, ranges from 0.10 to 10 wt% based on the weight of the modified polypropylene. For example, when the amount of the unsaturated carboxylic acid or derivatives thereof is less than 0.1 wt%, the intercalation effect of the modified polypropylene is low. On the other hand, when the amount is more than 10 wt%, a significant quantity of the modifier remains unreacted, causing problems in compatibility with polypropylene resin matrix.

The modified polypropylene preferably has a molecular weight of 1,000 to 500,000. For example, a modified polypropylene less than the lower limit in molecular weight deteriorates mechanical properties of the clay composite or cannot expand the interlayer space of layered clay minerals to a desired extent. On the other hand, in case the molecular weight exceeds 500,000, it is difficult for the modified polypropylene to penetrate the interlayer space of layered clay minerals because of a very high melt viscosity.

A preferable content of the modified polypropylene in the polypropylene-organic clay composite falls within the range from 1.0 to 30 wt%. When the content of the modified polypropylene is less than 1.0 wt%, an interface

joint strength between the organic layered clay mineral and the polypropylene resin cannot be maintained sufficiently to bring about neither intercalation effects nor improvements in mechanical properties of the polypropylene-organic clay composite. Whereas, when the modified polypropylene is contained in an amount of more than 30 wt%, mechanical properties of the polypropylene-organic clay composite is not further improved compared with those obtained with 30 wt%.

10 The organic layered clay mineral of the present invention means a layered clay mineral converted into organic mineral by organic onium ion. Representative examples of layered clay mineral used in the present invention include smectite-based, layered clay minerals such as montmorillonite, hectorite, saponite, nontronite and beidellite, vermiculite, and halloysite. A preferable layered clay mineral has electric charges and ions (e.g. sodium or calcium ion), preferably exchangeable by onium ion (e.g. ammonium cation), on their layers. Also, 20 preferable is a layered clay mineral whose contact area with the modified polypropylene having functional groups is large, because the interlayer space of layered clay mineral can be largely expanded thereby.

Generally, a cation exchange capacity of a negative charge on a surface of a layered clay mineral is 20 milliequivalents/100 g or more, and preferably 50 to 200 milliequivalents/100 g. In case the cation exchange capacity is less than 20 milliequivalents/100 g, a layered

clay mineral is not adequately converted into organic mineral by such ion exchange using organic onium ions, and so an interlayer space of the layered clay mineral is hardly expanded. While, in the case of more than 200 miliequivalents/100 g, an interlayer space of the layered clay mineral is not adequately expanded because organic onium ions have difficulty in penetrating an interlayer space of the layered clay mineral by ion exchange owing to strong bonding strength of the unit's particular layers of the layered clay mineral.

Organic onium ions are composed mainly of cation groups and lipophilic groups, wherein the cation groups play a role in exchanging ions on a surface of clay mineral, and the lipophilic groups allow organic substances to easily penetrate an interlayer space of the layered clay mineral by broadening the interlayer space of the layered clay mineral through their interaction with organic substances such as monomers or polymers. Generally, functional groups reacting to organic substances such as monomers or polymers, comprise nucleophilic or electrophilic functional groups which can be applied to electrophilic or nucleophilic displacement reactions, coupling reactions and ring-opening reactions. Examples of such functional group include epoxy, amino, carboxy, hydroxy, isocyanate, halogen, and epichloro hydrin.

Examples of the organic onium ion compound useful as an organic intercalant in the present invention include

quaternary ammonium salts with octadecyl, hexadecyl, tetradecyl or dodecyl groups, such as octadecyl trimethyl ammonium salt and ditetradecyl dimethyl ammonium salt. Preferably, the ammonium salts include bis(2-
5 hydroxyethyl)methyl octadecyl ammonium salt and dihydroxyethyl methylhydro ammonium salt.

While forming ionic bonds onto the surface of the clay mineral, the organic onium ions of the present invention are coupled with the modified polypropylene
10 through the reaction between the onium ions' terminal hydroxy or amino groups and the modified polypropylene's functional groups such as maleic anhydride groups.

The organic layered clay mineral is preferably contained in an amount of 1.0 to 20 wt% in the
15 polypropylene-organic clay composite. When the content of the organic layered clay mineral is less than 1.0 wt%, an improvement of mechanical properties of the polypropylene-organic clay composite cannot be expected, while, if it is more than 20 wt%, the mechanical
20 properties of the polypropylene-organic clay composite are not improved because the particles are hardly dispersed in nanometer size, but significantly aggregate.

Selected from crystalline isotactic polypropylene homopolymers and ethylene-propylene copolymers, the
25 polyolefin resin matrix ("c" component) of the present invention preferably ranges from 1.0 to 100 g/10 min in a melt index. For example, when the melt index of polyolefin resin matrix is below 1.0 g/10 min, the

composite is poor in moldability, resulting in low productivity of the molded products. On the other hand, when the melt index exceeds 100 g/10 min, the impact strength is drastically reduced.

5 A polypropylene-organic clay composite according to the present invention may comprise various other additives such as antioxidant, nucleating agent, lubricant, colorant, release agent, antistatic agent, and pigment. The type and amount of additives may be
10 determined depending on various factors including the desired usage and physical properties of the end products.

Also, the present invention pertains to a method for manufacturing the polypropylene-organic clay composite. In the method of the present invention, an organic
15 layered clay mineral, for example, a layered clay mineral with functional amino groups is reacted with a modified polypropylene having functional groups such as maleic anhydride in an inert solvent, or in a molten phase under a shearing force by using a mixer such as an extruder, a
20 Banbury mixer, etc.

The proper inert solvent may be hydrocarbon, e.g. benzene, toluene, xylene, for melting the modified polypropylene having functional groups. An organic layered clay mineral may be reacted with modified
25 polypropylene at a temperature of 100 to 120°C, which is high enough to melt both of the organic layered clay mineral and the modified polypropylene. The higher the temperature is, the faster the reaction is. The reaction

time depends on the degree of reaction of the two reactants.

The organic layered clay mineral is solution- or melt-mixed with the modified polypropylene as mentioned
5 above, followed by melt-kneading the resulting mixture along with a polyolefin resin matrix.

According to the present invention, the melt-kneading is carried out with the use of an extruder, a Banbury mixer, or a Brabender mixer under a mechanical
10 shearing force at the polymer's melting point or a higher temperature.

The method according to the present invention has advantages in that more tie chains exist between the polypropylene crystals of the composite of the present
15 invention. These tie chains function to connect the polypropylene crystals to each other to increase the interface joint strength, leading to an increase in modulus and tensile strength when stress or a deformation is applied to the polymers. Additionally, the crack
20 growth in the final product requires a cutting of the tie chains existing between opposite crystalline sides of the ruptured portion of the polypropylene. Therefore, a quantitative increase in tie chains disturbs the growth of the crack.

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A more detailed description of the present invention will be given in conjunction with the following examples. The following examples are for illustration purposes only

and in no way limit the scope of this invention.

The following examples 1 to 12 are accomplished according to the present invention, and comparative examples 1 to 10 are disclosed in comparison with the present invention. Compositions of respective components and mechanical properties of the resulting composites according to examples and comparative examples are described in Tables 1 to 3.

Respective components used in examples 1 to 12 and comparative examples 1 to 10 are defined as follows:

1) polypropylene: ethylene-propylene block copolymer with a melt index (MI) of 5 g/10 min (230°C).

2) montmorillonite (1): montmorillonite whose cations were exchanged with methyl, tallow, and bis 2-hydroxyethyl ammonium chloride. This clay may be commercially available from Southern Clay Products, Inc., Texas, and has a cation exchange capacity of 90 miliequivalents/100 g, and an interlayer space of 18 Å.

3) montmorillonite (2): sodium montmorillonite, manufactured by Southern Clay Products, Inc., Texas, with an interlayer space of 11 Å.

4) montmorillonite (3): based on the sodium montmorillonite of Southern Clay Products, Inc., Texas. Its cations were exchanged with alkylammonium cations, such as stearyl amine and 1,6-diaminehexane.

Montmorillonite (3), used as organic clay in the present invention, was prepared as follows. Sodium

montmorillonite was suspended in warm water of 80°C with stirring by use of a homogenizer. In water of 80°C in another vessel were dissolved stearyl amine, 1,6-diaminohexane, and conc-HCl. An ammonium salt solution
5 was poured into the sodium montmorillonite suspension. Subsequently, the resulting mixture was stirred by use of a homogenizer for 10 min, washed with water of 80°C three times, filtered, and then dried in a vacuum oven at 80°C for 24 hours. The interlayer space of the layered
10 minerals was analyzed to be 19 Å as measured by X-ray diffractometer.

Taking advantage of its compatibility with the main chain of polypropylene having functional groups, the stearyl amine was used in order to improve the
15 intercalation effect between clay mineral particular layers. As for 1,6-diaminehexane, its aim was to increase the interface joint strength between clay mineral particular layers through the reaction with the functional groups of the modified polypropylene so as to
20 maximally improve mechanical properties of the resulting polypropylene-organic clay composite.

5) modified polypropylene (1): polypropylene containing reacted glycidyl methacrylate of 3.0 wt% based on the weight of polypropylene.

25 6) modified polypropylene (2): polypropylene containing reacted glycidyl methacrylate of 0.1 wt% based on the weight of polypropylene.

7) modified polypropylene (3): polypropylene

containing reacted maleic anhydride of 2.0 wt%.

8) modified polypropylene (4): polypropylene containing reacted maleic anhydride of 0.1 wt%.

9) modified polypropylene (5): polypropylene
5 containing reacted maleic anhydride of 3.0 wt%.

EXAMPLES 1 TO 3

Modified polypropylene (1), along with an
10 antioxidant, was completely dissolved in 2000 ml of toluene at 100°C and added with montmorillonite (1) according to the compositions given in Table 1 below, followed by vigorously stirring the resulting mixture for at least 4 hours. Afterwards, the resulting mixture was
15 precipitated in 3000 ml of acetone at room temperature. The precipitate thus obtained was dried in a vacuum oven at 100°C for at least 12 hours to give a conjugate in which glycidyl methacrylate polypropylene was coupled onto the surface of the organic clay mineral through an
20 ester or hydroxyl group. This was confirmed through analysis of the resulting compound by IR spectroscopy and NMR spectrometry.

The organic clay compound was dry-blended with polypropylene and additives in a Hensel mixer and the
25 mixture was added into a main hopper of an SW TEX44ALPHA twin screw kneading extruder at once, and melt-kneaded to prepare a composite. The dispersibility of the clay particles was confirmed through measurement of the

interlayer space of layered clay mineral in a composite specimen by X-ray diffractometry. The dispersed state of the layered clay particles in the composite was also examined with the aid of transmission electron microscope (TEM). The resulting composite was injected through FCM-110 (with a mould clamping force of 110 ton), manufactured by Samsung Kleokner, to produce a specimen according to the American Society for Testing & Materials (ASTM), and measured for mechanical properties, such as flexural modulus, heat deflection temperature and Izod impact strength.

EXAMPLE 4

Modified polypropylene (1) was dry-blended with montmorillonite (1) according to the composition given in Table 1 below, and then the resulting mixture was melt-kneaded with the use of a kneader blender to prepare a organic clay compound masterbatch. Afterwards, the organic clay compound was dry-blended again with polypropylene and additives in a Hensel mixer, and the resulting mixture was added into a main hopper of an SW TEX44ALPHA twin screw kneading extruder at once, and melt-kneaded to prepare a composite.

25

EXAMPLES 5 TO 7

Modified polypropylene (3), along with an

antioxidant, was completely dissolved in 2000 ml of xylene at 100 to 120°C and added with montmorillonite (1) according to the compositions given in Table 2 below, followed by vigorously stirring the resulting mixture for
5 at least 4 hours. Afterwards, the resulting mixture was precipitated in 3000 ml of acetone at room temperature. The precipitate thus obtained was dried in a vacuum oven at 100°C for at least 12 hours to give a conjugate in which maleitide polypropylene was coupled onto the
10 surface of the organic clay mineral through an ester group. This was confirmed through analysis of the resulting compound by IR spectroscopy.

The organic clay compound was dry-blended with polypropylene and additives in a Hensel mixer and the
15 mixture was added into a main hopper of an SW TEX44ALPHA twin screw kneading extruder at once, and melt-kneaded to prepare a composite. The dispersibility of the clay particles was confirmed through measurement of the interlayer space of layered clay mineral in a composite
20 specimen by X-ray diffractometry. The dispersed state of the layered clay particles in the composite was also examined with the aid of transmission electron microscope (TEM). The resulting composite was injected through FCM-110 (with a mould clamping force of 110 tons),
25 manufactured by Samsung Kleokner, to produce a specimen according to the American Society for Testing & Materials (ASTM), and measured for mechanical properties, such as flexural modulus, heat deflection temperature and Izod

impact strength.

EXAMPLE 8

5 Modified polypropylene (3) was dry-blended with
montmorillonite (1) according to the composition given in
Table 2 below, and then the resulting mixture was melt-
kneaded with the use of a kneader blender to prepare a
organic clay compound masterbatch. Afterwards, the
10 organic clay compound was dry-blended again with
polypropylene and additives in a Hensel mixer, and the
resulting mixture was added into a main hopper of an SW
TEX44ALPHA twin screw kneading extruder at once, and
melt-kneaded to prepare a composite.

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COMPARATIVE EXAMPLES 1 TO 7

Montmorillonite alone, or montmorillonite
concomitant with modified polypropylene was dry-blended
20 with polypropylene and additives in a Hensel mixer, and
the resulting mixture was added into a main hopper of an
SW TEX44ALPHA twin screw kneading extruder at once, and
melt-kneaded to prepare a composite.

25 Each composite specimen was measured for the
interlayer space of layered clay mineral and for the
dispersed state of layered clay particles as follows:

1) X-ray diffractometry: RINT-2000, manufactured by

Rigakku Co., Japan, was used with CuK α (λ = 0.15 nanometer) ray.

2) Transmission electron microscope (TEM): Using JEOL 2000EX, observation was made at an accelerating voltage of 100 kV. A specimen was manufactured by dyeing with ruthenium tetroxide a thin flake cut by a microtome. Observed results were evaluated in O or X. O means good dispersibility. In this regard, the particles of the layered clay mineral were invisible to the naked eye and were well dispersed in the matrix as demonstrated by the analysis of TEM. Also, the interlayer space of the layered clay mineral was widened 10 times or more in comparison with that of the original layered clay mineral as observed by TEM. X means poor dispersibility such that the particles of the layered clay mineral were visible to the naked eye. Further, the analysis of TEM showed that the particles were aggregated and the interlayer space of the layered clay mineral was widened less than 10 times in comparison with that of the original layered clay mineral.

Test conditions for mechanical properties were as follows:

1) Flexural modulus

It was measured at room temperature according to American Society for Testing & Materials (ASTM) D790.

2) Heat deflection temperature

It was measured under a low load (4.6 kg) according to American Society for Testing & Materials (ASTM) D648.

3) Izod impact strength

It was measured at room temperature with the use of a notch specimen according to American Society for Testing & Materials (ASTM) D256.

TABLE 1

	Example	Comp. Exam.						
		1	2	3				
Composition (wt%)	polypropylene	86.6	79.9	73.2	86.6	100	93.3	73.2
	montmorillonite(1)	6.7	6.7	6.7	6.7	-	6.7	-
	montmorillonite(2)	-	-	-	-	-	-	6.7
	denatured polypropylene(1)	6.7	13.4	20.1	6.7	-	-	-
	denatured polypropylene(2)	-	-	-	-	-	-	20.1
Dispersibility	interlayer space(Å)	51	57	67	42	-	19	13
	disperse state	0	0	0	0	-	X	X
Mechanical properties	flexural modulus(Mpa)	2160	2270	2440	2080	1350	1680	1730
	heat deflection temperature(°C)	121	118	116	114	102	107	106
	Izod impact strength(J/m)	121	117	111	104	130	88	69

TABLE 2

	Example	Comp. Exam.							
		5	6	7	8	4	5	6	7
Composition (wt%)	polypropylene	85.8	78.7	71.6	85.8	100	92.9	92.9	71.6
	montmorillonite(1)	7.1	7.1	7.1	7.1	-	7.1	-	-
	montmorillonite(2)	-	-	-	-	-	-	7.1	7.1
	denatured polypropylene(3)	7.1	14.2	21.3	7.1	-	-	-	21.3
	denatured polypropylene(4)	-	-	-	-	-	-	-	-
Dispersibility	interlayer space(Å)	52	65	68	43	-	19	12	15
	disperse state	0	0	0	0	-	X	X	X
Mechanical properties	flexural modulus (Mpa)	2400	2580	2640	2180	1450	1720	1770	1790
	heat deflection temperature (°C)	126	125	122	119	105	108	107	106
	Izod impact strength(J/m)	67	64	62	63	72	38	30	26

As apparent from the results shown in Tables 1 and 2, it can be seen that the composites prepared in examples 1 to 8 are better than those prepared in comparative examples 1 to 7 in terms of dispersibility and mechanical properties. That is, the composites of examples 1 to 8 had the layered clay minerals with longer interlayer space and showed better flexural modulus, heat deflection temperature, which represents a degree of heat resistance, and Izod impact strength than those of comparative examples 1 to 7.

EXAMPLES 9 TO 11

Modified polypropylene (5), along with an antioxidant, was completely dissolved in 2000 ml of toluene at 100°C and added with montmorillonite (3) according to the compositions given in Table 3 below, followed by vigorously stirring the resulting mixture for at least 4 hours. Afterwards, the resulting mixture was precipitated in 3000 ml of acetone at room temperature. The precipitate thus obtained was dried in a vacuum oven at 80°C for at least 24 hours to give a conjugate in which the modified polypropylene (5) was coupled to an amine group on the surface of the organic clay mineral to form an amide bond. This was confirmed through analysis of the resulting compound by IR spectroscopy and NMR spectrometry.

The organic clay compound was dry-blended with

polypropylene and additives in a Hensel mixer and the mixture was added into a main hopper of an SW TEX44ALPHA twin screw kneading extruder at once, and melt-kneaded to prepare a composite. The dispersibility of the clay particles was confirmed through measurement of the interlayer space of layered clay mineral in a composite specimen by X-ray diffractometry. The dispersed state of the layered clay particles in the composite was also examined with the aid of transmission electron microscope (TEM). The resulting composite was injected through FCM-110 (with a mould clamping force of 110 tons), manufactured by Samsung Kleokner, to produce a specimen according to the American Society for Testing & Materials (ASTM), and measured for mechanical properties, such as flexural modulus, heat deflection temperature and Izod impact strength.

EXAMPLE 12

Modified polypropylene (5) was dry-blended with montmorillonite (3) according to the composition given in Table 3 below, and then the resulting mixture was melt-kneaded with the use of a kneader blender to prepare a organic clay compound masterbatch. Afterwards, the organic clay composition was dry-blended again with polypropylene and additives in a Hensel mixer, and the resulting mixture was added into a main hopper of an SW TEX44ALPHA four screw kneading extruder at once, and melt-kneaded to prepare a

composite.

COMPARATIVE EXAMPLES 8 TO 10

5 Montmorillonite alone, or montmorillonite
concomitant with modified polypropylene was dry-blended
with polypropylene and additives in a Hensel mixer, and
the resulting mixture was added into a main hopper of an
SW TEX44ALPHA twin screw kneading extruder at once, and
10 melt-kneaded to prepare a composite.

Each composite specimen was measured for the
interlayer space of the layered clay mineral and for the
dispersed state of the layered clay particles by X-ray
diffractometry and transmission electron microscope
15 (TEM), respectively, under the same analysis conditions
as those of examples 1 to 8 and comparative examples 1 to
7.

In addition, measurement was made of the mechanical
properties of the resulting composites, including
20 flexural modulus and Izod impact strength, under the same
analysis conditions as those of examples 1 to 8 and
comparative examples 1 to 7.

TABLE 3

	Example					Comp. Exam.						
	9	10	11	12		8	9	10				
Composition (wt%)	Polypropylene					85.2	77.8	70.4	85.2	100	92.6	70.4
	montmorillonite(2)					-	-	-	-	-	-	6.7
	montmorillonite(3)					7.4	7.4	7.4	7.4	-	7.4	-
	denatured polypropylene(4)					-	-	-	-	-	-	22.2
	denatured polypropylene(5)					7.4	14.8	22.2	7.4	-	-	-
Dispersibility	interlayer space(Å)					68	69	77	46	-	22	13
	disperse state					0	0	0	0	-	X	X
Mechanical properties	flexural modulus(Mpa)					2300	2380	2510	2110	1350	1640	1760
	Izod impact strength(J/m)					123	112	107	102	130	82	63

As apparent from the results shown in Table 3, it can be seen that the composites prepared in examples 9 to 12 are better than those prepared in comparative examples 8 to 10 in terms of dispersibility and mechanical properties. That is, the composites of examples 9 to 12 had the layered clay minerals with longer interlayer space and showed better flexural modulus and Izod impact strength than those of comparative examples 8 to 10.

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Industrial Applicability

As stated above, the polypropylene-organic clay composite of the present invention is excellent in mechanical properties, such as rigidity, heat resistance and impact resistance, by virtue of the excellent dispersibility of the organic clay mineral particles. Also, the excellent dispersibility endows the composite with good fire retardancy, transparency, and gas and liquid impermeability. With these advantages, the polypropylene-organic clay composite of the present invention can be molded into slim and light products, which find numerous applications in various industries, including automobiles, industrial materials, and electrical and electronic appliances.

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Claims

1. A polypropylene-organic clay composite comprising:

- 5 (a) 1.0 to 30 wt% of a modified polypropylene having functional groups;
- (b) 1.0 to 20 wt% of an organic layered clay mineral connected chemically to the functional group of said modified polypropylene; and
- 10 (c) 50 to 98 wt% of a polyolefin resin matrix in which said modified polypropylene and said organic layered clay mineral are dispersed.

2. The polypropylene-organic clay composite
15 according to claim 1, wherein said modified polypropylene is polypropylene homopolymer, ethylene/propylene copolymer, or propylene/ α -olefin non-conjugated diene compound copolymer, having a melt index (MI) of 1.0 to 100 g/10 min, and being modified by unsaturated
20 carboxylic acid or derivative thereof.

3. The polypropylene-organic clay composite according to claim 2, wherein said unsaturated carboxylic acid or derivative thereof is selected from a group
25 consisting of maleic anhydride, itaconic anhydride, ditraconic anhydride, oxalic acid, glycidyl methacrylate, carboxylic acid ester, carboxylic acid ether or thiocarboxylic acid.

4. The polypropylene-organic clay composite according to claim 2, wherein said unsaturated carboxylic acid or derivative thereof is maleic anhydride or glycidyl methacrylate.

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5. The polypropylene-organic clay composite according to any one of claims 2 to 4, wherein an amount of said unsaturated carboxylic acid or derivative thereof ranges from 0.10 to 10 wt% based on polypropylene.

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6. The polypropylene-organic clay composite according to claim 1, wherein said organic layered clay mineral is a clay mineral converted into organic mineral by an organic onium ion compound.

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7. The polypropylene-organic clay composite according to claim 6, wherein said organic layered clay mineral is selected from a group consisting of montmorillonite, hectorite, saponite, nontronite, beidellite, vermiculite, and halloysite.

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8. The polypropylene-organic clay composite according to claim 6, wherein said organic onium ion compound is ammonium salt.

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9. The polypropylene-organic clay composite according to claim 1, wherein said polyolefin resin is polypropylene.

10. A method for manufacturing the polypropylene-organic clay composite of claim 1, comprising the steps of:

5 reacting a modified polypropylene having functional groups to an organic layered clay mineral in a solvent or in a molten phase under a shearing force; and

10 melt-kneading the mixture of the modified polypropylene and the organic layered clay mineral with a polyolefin resin matrix under a shearing force.

INTERNATIONAL SEARCH REPORT

International appl.
PCT/KR01/01098

A. CLASSIFICATION OF SUBJECT MATTER

IPC7 C08K 3/34, C08L 23/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7 C08K, C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the files searched

KR, JP: IPC as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 10-182892 A (Toyota Central Res & Dev Lab Inc.) 7 July 1998 cited in the application See the whole document	1 - 10
P, X	JP 2000-281841A (Nippon Polyofefin K.K.) 20 October 2000 See the whole document	1 - 10
A	JP 7-102124 A (Showa Denko K.K.) 18 April 1995 See the whole document	1 - 10
A	JP 54-68852 A (Idemitsu Kosan Co., Ltd.) 2 June 1979 See the whole document	1 - 10

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "&" document member of the same patent family

Date of the actual completion of the international search

11 OCTOBER 2001 (11.10.2001)

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12 OCTOBER 2001 (12.10.2001)

Name and mailing address of the ISA/KR

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